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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Nanotomography of hierarchically organized porous silica monoliths: a necessary step towards quantification of sorption induced deformation at all scales	**Experiment number**: MA-3767
Beamline: ID16-A	**Date of experiment**: from: 28/09/17 to: 02/10/17	**Date of report**: 23/02/18
Shifts: 12	**Local contact(s)**: Julio Da Silva	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

In this experiment, we have used high-resolution tomography at beamline ID 16A to characterise the morphology of a new hierarchically organised silica material consisting of a macroporous network of mesoporous crystallites. This material deforms reversibly upon fluid adsorption [1] but modeling and thus predicting the deformation [2] was so far not possible because a thorough description of the 3D network of crystallites had been lacking.

The samples consisted of nine bulk samples from which small needles had been cut free using a precision saw. The needles had a roughly square cross section of around 100 µm in width. These were broken off with part of the bulk substrate and transferred to Huber pins. Three of the samples were expected to have a spatially isotropic network structure whereas three others had been treated to exhibit a preferential direction in the network. The last set of samples were carbon negatives produced using the mesopores in the crystallites as templates and subsequently etching the silica matrix away.

For recording tomographic data on our samples, we used the holotomography setup, i.e. a high-resolution imaging detector lens-coupled to a FReLoN F_K4320 (2048x2048 pixels, 1.1 um pixel size) and scanned the samples at four distances to the detector to retrieve the best possible result. The scans generally took about four hours per sample and we performed the data reconstruction in parallel. For all of the nine sample, we were able to record at least one data set but on several we did a scan at lower resolution and larger field of view (40 or 30 nm voxel size) first and then zoomed into a region of interest at 10 nm voxel size. Accounting for sample preparation and sample changing procedure as well as a downtime of the beam of several hours, we were able to utilize the allocated four days of beamtime nearly optimally and recorded a total of thirteen data sets.

The figure below shows slices of the reconstructed tomography data for an isotropic silica sample and its carbon negative at two different resolutions. In both cases the network (dark grey) of mesoporous crystallites and respectively their carbon negative is visible. The image quality however is somewhat better in the left side of the figure as noise is reduced and contrast between the network and the background is higher. The reason for the higher noise levels in the right side of the figure is probably due to vibrations. Furthermore, the beamline staff had been tweaking the acquisition procedure during the beamtime so that the results for the latter samples (i.e. the carbon negatives) had been improved.

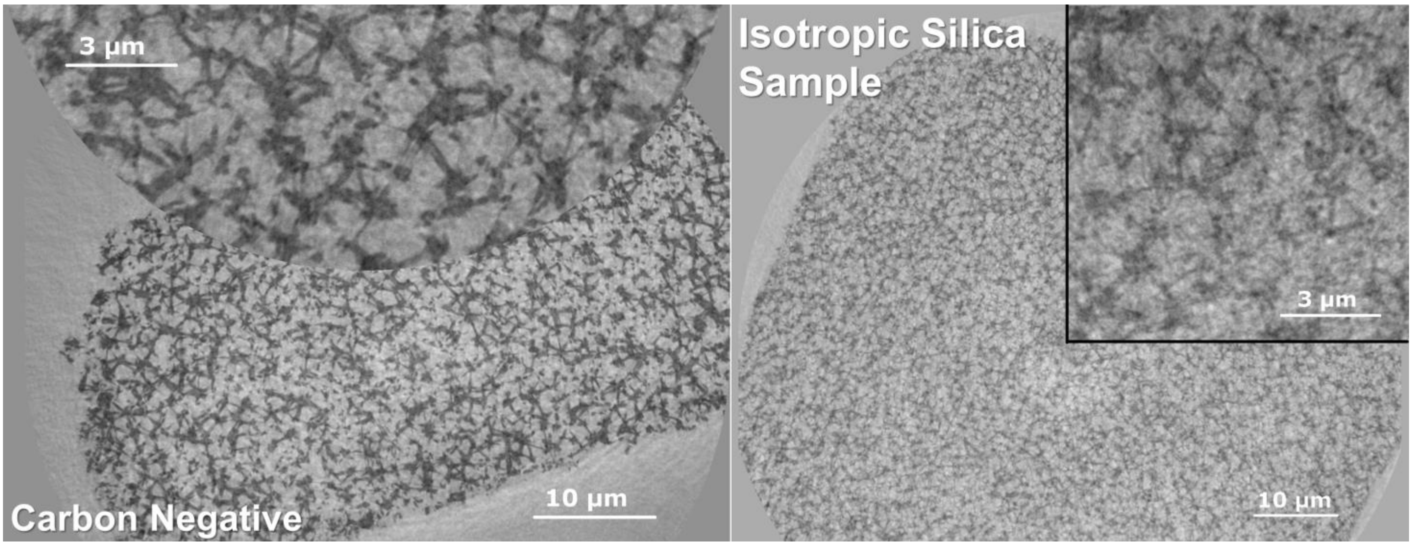

Figure: Slices of reconstructed tomography data for two samples at two different resolutions: voxel sizes 40/30 nm (bottom right/left) and 10 nm (top).

We have started to process the data and can conclude that for most data sets the quality of the data is more than sufficient to confidently extract the crystallite network. The data sets with poorer image quality will be treated to enhance contrast and reduce noise. Thus, all the data sets will be used in finite element modelling to simulate the deformation of the network upon fluid sorption and combined with small-angle x-ray scattering data to further understand the interplay between deformation of the individual mesopores in a crystallite and the entire network of crystallites. For the presumed anisotropic samples, we found only one data set that visually shows a high degree of anisotropy but further analysis, e.g. calculating the preferential directions in the sample, might show a lesser degree of anisotropy for the other samples. Furthermore, we have presented our first attempts at treating and segmenting the data at the 2018 ESRF User Meeting on a poster entitled "*Nanotomography of Hierarchically Organized Porous Silica Monoliths*".

[1] Balzer C, Morak R, Erko M, Triantafillidis C, Husing N, Reichenauer G, Paris O, Relationship Between Pore Structure and Sorption-Induced Deformation in Hierarchical Silica-Based Monoliths. Z Phys Chem. 2015 Aug;229(7-8):1189-209.

[2] Balzer C, Waag A, Gehret S, Reichenauer G, Putz F, Huesing N, Paris O, Bernstein N, Gor GY, Neimark AV, Adsorption-induced deformation of hierarchically-structured mesoporous silica - effect of local anisotropy. Langmuir. 2017(33): 5592–5602.